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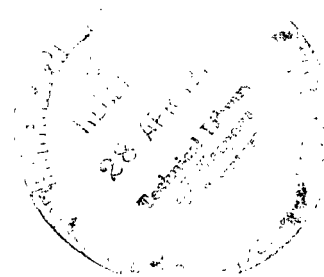
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OXIDATION OF Ni-20Cr-2ThO_2 AND Ni-30Cr-1.5Si AT 800° , 1000° , AND 1200° C

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16. Abstract High-temperature X-ray diffraction, weight- and thickness-change measurements, and electron-microprobe analysis were combined to study oxidation of Ni-20Cr-2ThO ₂ (TD-NiCr) and Ni-30Cr-1.5Si (Tophet-30) in static air for 100 hours. Oxidation after grinding the surface of TD-NiCr gave a Cr ₂ O ₃ scale, while oxidation after polishing gave a scale of NiO, NiCr ₂ O ₄ , and Cr ₂ O ₃ . Cr ₂ O ₃ was lost by vaporization from both scales extensively, but the polished material was somewhat more oxidation resistant. After either surface preparation, Tophet-30 formed a Cr ₂ O ₃ scale which seemed more resistant to vaporization loss than the Cr ₂ O ₃ on TD-NiCr. Metal-thickness losses were similar in both alloys.					
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SUMMARY

High-temperature X-ray diffraction, weight-change and thickness-change measurements, electron-microprobe analysis, and metallography were combined in a study of the static-air oxidation of TD-NiCr (Ni-20Cr-2ThO₂) and Tophet-30 (Ni-30Cr-1.5Si). Surface preparation, exposure time, and exposure temperature were variables. Test times up to 1000 hours were used for the metal-thickness-change experiments but were 100 hours for the rest of the work. The temperatures were 800°, 1000°, and 1200° C.

An effect of surface preparation on subsequent oxidation behavior of TD-NiCr was noted. Polished specimens first formed NiO, closely followed by Cr₂O₃. With time, NiCr₂O₄ formed from the reaction of NiO and Cr₂O₃. Concurrently, Cr was dissolved in the outer NiO layer, from which chromium was lost by vaporization. Ground TD-NiCr specimens formed only Cr₂O₃, which was also lost by vaporization. Both kinds of specimens were highly oxidation resistant under the isothermal furnace conditions investigated.

Measurements of the change in metal thickness as a result of oxidation led to the conclusion that the polished TD-NiCr oxidized somewhat less than the ground material at 1200° C. For example, after 1000 hours at 1200° C, the ground sample lost about 30 micrometers, while the electropolished sample lost about 20 micrometers.

Tophet-30 oxidized in a manner independent of surface preparation. The only major oxide phase was Cr₂O₃, although minor amounts of SiO₂ were found at 1000° and 1200° C. Tophet-30 gained more weight than TD-NiCr, but the change in metal thickness due to oxidation was about the same as, or a little more than, the ground TD-NiCr (~40 μm) at 1200° C for 1000 hours. In addition, Tophet-30 oxidized internally (to a depth of ~140 μm at 1200° C for 1000 hr).

INTRODUCTION

The nickel-chromium system has formed the basis for superalloys and heater materials for many years (refs. 1 and 2). Indeed, heat-resisting alloys with compositions near 80Ni-20Cr can be traced back to 1906. Since this time, many investigations of the oxidation resistance of this and similar systems have been made.

Unfortunately, there is much conflicting evidence resulting from the oxidation studies of these systems. In particular, many investigators have concluded that Cr_2O_3 is the protective scale which imparts oxidation resistance to this class of material, while many others have concluded that the protective scale is NiCr_2O_4 (e.g., see refs. 1 and 3 to 5). Some of these discrepancies may have arisen from uncontrolled or ill-defined variables such as specimen purity and surface preparation. Both these variables have been shown to control the oxides formed (refs. 6 to 8).

The alloys in this program are nickel-chromium alloys, one of which is a relatively new dispersion-strengthened nickel alloy (TD-NiCr), while the other is an older alloy (Tophet-30) developed for use as a heating element in electric resistance furnaces. TD-NiCr (Ni-20Cr-2ThO₂) is of interest in advanced airbreathing engines because of its good high-temperature mechanical properties and relatively good oxidation resistance. Tophet-30 (Ni-30Cr-1.5Si) has good oxidation resistance, but it lacks adequate strength for gas-turbine components. It is, however, being considered as a cladding for stronger superalloys (ref. 9).

The objectives of this study were twofold. The first was to determine the effects of time, temperature, and surface preparation on the severity of oxidation of TD-NiCr and Tophet-30. The second was to determine the composition and morphology of the oxide scales formed during oxidation. The temperature range of the work was 800° to 1200° C for times to 1000 hours. The oxidizing medium was static air at 1-atmosphere pressure.

To achieve these objectives, several techniques were used. The procedures were similar to those used by two of the authors in studying the oxidation of WI-52, a cobalt-based superalloy (ref. 6):

- (1) Weight change (ΔW)
- (2) High-temperature X-ray diffraction (HTXRD)
- (3) Room-temperature X-ray diffraction (XRD), electron microprobe analysis (EMP), and metallography

In addition, thickness-change measurements (Δt) were made. This was necessitated by the vaporization of chromium oxide from the scales (ref. 10), which made interpretation of the weight-change data tenuous. The thickness-change measurements were, in themselves, difficult to make in these highly oxidation-resistant alloys because little change was detected even after exposures up to 1000 hours at 1200° C.

MATERIALS

Both alloys were received as 0.100-inch (0.254-cm) thick cold-rolled sheets. Their analyses, as determined by wet chemical and spectrographic means, are shown in table I. Both alloys were close to their nominal compositions. The Cr content of the Tophet-30 was about 29.6 percent, while that of the TD-NiCr was about 21.7 percent. Of special note is the relatively high purity of the TD-NiCr as compared to the Tophet-30, which contains nearly 0.7 percent impurities.

Electron-metallography (figs. 1(a) and (b)) revealed that, in the as-received condition, both solid-solution alloys contained additional phases. This was, of course, expected for the TD-NiCr, as fine particles of ThO_2 are intentionally added to strengthen the matrix; in figure 1(a), some of the larger particles were probably Cr_2O_3 , since this phase was detected by X-ray diffraction. The additional phases (one platelet and one feathery, as shown in fig. 1(b)) in Tophet-30 were more difficult to identify. XRD of bulk specimens did not give any identifiable patterns due to the small volume percents of the minor phases. Extraction with HCl-methanol solutions followed by spectrographic and XRD analyses led to an identification of one of the phases as ZrC with a lattice parameter a_0 of $4.714 \pm 0.005 \text{ \AA}$. The other phase was present in such small amounts that even with this technique the pattern obtained for this phase could not be identified. A likely possibility would be SiC.

SURFACE PREPARATION

Two surface preparations were used in this work. Previous work at Lewis (refs. 6 and 7) and Stanford Research Institute (ref. 11) indicated that surface preparation has a major effect on the oxidation of chromium-bearing alloys. In this study, an effort was made to select two extremes in surface preparation: surface grinding and metallographic polishing. Surface-ground samples were formed with a 70-grit SiC wheel, while the polished samples were finished with 0.5-micrometer diamond. Both surfaces had rms roughness values of 1 to 3 microinches (2.5×10^{-6} to 7.6×10^{-6} cm). However, the X-ray patterns of the ground samples showed considerable line broadening, which could be evidence of either surface strain or a small crystallite size on the surface. Specimens with both surface conditions were used in HTXRD, ΔW , and Δt analyses. Before oxidation, all surfaces were given a final cleaning with alcohol.

The HTXRD samples were cut into rectangular plates 0.375 inch by 0.500 inch (0.95 cm by 1.27 cm). The ΔW and Δt samples were cut into rectangular plates 0.750 inch by 1.00 inch (1.90 cm by 2.54 cm). In all cases, the initial thicknesses were not changed, except by surface preparation.

EQUIPMENT AND PROCEDURE

Weight-Change Experiments (ΔW)

The equipment and procedure used for continuous weight-change measurements were similar to those of reference 6. The apparatus is shown in figure 2. A sample was suspended from a recording balance whose sensitivity was 0.2 milligram. The sample was brought to temperature by raising a wire-wound furnace to surround the sample. The inner lining of the furnace was a tube of high-density alumina. The sample took approximately 10 minutes to reach temperature after the furnace was raised. After 100 hours at temperature the furnace was lowered and the sample was allowed to cool. A pyrex beaker was positioned around the sample to catch any spall. After a few hours the sample was removed from the beaker and mounted for metallographic and EMP examination.

Thickness-Change Experiments (Δt)

Prior to oxidation tests, the thickness of the ground and/or polished samples was measured with a bench micrometer to a precision of ± 0.0001 centimeter. Samples of each surface preparation were suspended together in a furnace.

Two exposure temperatures, 1000° and 1200° C, were used. To achieve sufficient oxidation for a measurable thickness change, test times approaching 1000 hours were necessary. After these exposures, the samples were fastened to guide blocks to ensure vertical positioning and were mounted in epoxy. The samples were cut in half, with care taken to index to the mounting blocks to prevent cutting at an angle. Residual-metal thickness was measured with both an optical comparator and a microhardness microscope to a precision of ± 0.0002 centimeter.

High-Temperature X-Ray Diffraction (HTXRD)

The apparatus used in HTXRD has been described in detail in reference 12, and is shown schematically in figure 3. Briefly, this technique involved heating a thermocoupled sample on a close-fitting shaped platinum strip heater. This assembly was placed at the sample position of a vertical diffractometer. The sample was heated to the oxidation temperature in less than 5 minutes; diffractometer scans were made frequently in the first stages of oxidation and then less frequently as the oxidation rate slowed. At the conclusion of each run (100 hr), the temperature was lowered in 200° C steps. Patterns were run at each stage to check for possible phase changes. When the sample reached room temperature, it was removed and examined by standard XRD and metallography.

Room-Temperature X-Ray Diffraction (XRD), Electron Microprobe Analysis (EMP), and Metallography

Room-temperature XRD was done both on the in situ scales and on material removed from the surface with a diamond drill. The latter approach produced powders which were run in a 11.46-centimeter-diameter Debye camera which utilized Straumanis-type film loading. The in situ scales were run on a horizontal diffractometer which had a diffracted-beam monochromator. All X-ray work was done with Cu K radiation.

The EMP unit had a three-channel capacity, to allow simultaneous analysis of three elements. Samples were traversed from the metal through the scale.

Metallographic examinations were made prior to EMP analysis. Samples were examined unetched in most cases.

RESULTS AND DISCUSSION

Oxidation of TD-NiCr

Weight change (ΔW). - As shown in figure 4, surface preparation had a noticeable effect on the oxidation of TD-NiCr. The ground samples gained less weight than the electropolished samples at all temperatures. At 800^o C, ground TD-NiCr gained weight linearly for the entire 100 hours, while at 1000^o C there was slight weight increase for about 20 hours and then no further change was detected. At 1200^o C, a rapid weight gain was measured for about 1 hour and then the sample lost weight linearly until the conclusion of the test. Curves for all the electropolished samples had the same shape, an initially rapid weight gain followed by little, if any, weight change after 10 hours. The 1000^o C and 1200^o C samples spalled slightly upon cooling. In all cases the final weight gains appeared to be inversely related to the temperature. This result is consistent with Douglass's work on electropolished TD-NiCr (ref. 11). For comparison, other weight-change data for 80Ni-20Cr are also plotted in figure 4. In contrast to the present work, both references 5 and 13 yield data which are nearly parabolic. The data are from commercial heater alloys, however, not pure 80Ni-20Cr.

Thickness change (Δt). - All ΔW samples were checked for changes in metal thickness, but these few measurements proved insufficient due to the very small amount of metal consumed in the 100-hour tests. This is indicative of the excellent oxidation resistance of TD-NiCr under the conditions of our tests. Therefore, samples were prepared specifically for Δt measurements and exposed for times as long as 1000 hours (see table II). These long-time tests indicated that the ground material lost slightly

more metal than the polished samples at 1200° C, while the 1000° C data remained inconclusive even at 1000 hours. In addition, the uncertainties of the values for the polished samples are greater than those for the ground samples. This is due to the sample becoming slightly tapered during the polishing operations. This taper made initial thickness measurements difficult, while uncertainties in the position of the final measurement compounded the error.

High-temperature X-ray diffraction (HTXRD). - X-ray diffraction studies clearly reflected differences in oxidation behavior due to surface preparation. Unlike the scales formed on IN-100 and WI-52 (see ref. 12), the oxides found on TD-NiCr and Tophet-30 show preferred orientation. Furthermore, the degree of preferred orientation changed over the course of some runs. In an attempt to minimize the influence of this effect on the diffraction data, the peak intensities of several diffraction lines were summed for each oxide and plotted as a function of time in figures 5 to 9. Thus, the effects of diminution of some lines and enhancement of others due to preferred orientation could be reduced by the appropriate choice of lines. The curves are meant to show trends only and are not meant to be quantitative. A fuller discussion of these points is presented in reference 12. In addition to the oxides in the scales, ThO₂ and the nickel solid-solution lines were also plotted. The presence of the nickel solid-solution lines gave assurance that complete penetration of the oxide was effected. The ThO₂ plot was made in an effort to determine whether this oxide was concentrated in the scale or overlaid by the scale.

The ground surface, studied at 1000° and 1200° C, produced the simpler system of oxide growth and is treated first. At 1000° C (see fig. 5), only Cr₂O₃ formed throughout the entire 100-hour run. This observation agrees with Barrett (ref. 5) but not with Wood and Hodgkiess, who found NiO and possibly NiCr₂O₄ (ref. 3). (Ref. 3 does not deal specifically with an 80Ni-20Cr alloy, but it does have results obtained on alloys with both more and less than 20 percent chromium.) After about 50 hours, there was a slight decrease in the Cr₂O₃ intensity, with a corresponding increase in the ThO₂ intensity. The decrease in the Cr₂O₃ offers evidence for loss of Cr₂O₃ due to volatility (ref. 10). The Ni solid-solution pattern was strong throughout; it was plotted on a separate scale because of its much higher intensity.

At 1200° C, the tendency for Cr₂O₃ loss was still present at times approaching 100 hours (see fig. 6). In fact, the loss proceeded to the point where NiO and NiCr₂O₄ began to form as a result of chromium depletion from the alloy. The ThO₂ intensity rose sometime around 50 hours at nearly the same time that NiO and NiCr₂O₄ began to appear. This may indicate that the ThO₂ was in the NiO-NiCr₂O₄ part of the scale and not in the Cr₂O₃, or it may just reflect a reduction in the thickness of the Cr₂O₃ overlaying it. In either event, it seems that little ThO₂ was in the Cr₂O₃.

The polished samples - at 800°, 1000°, and 1200° C - showed more complex behavior, which was more nearly like that anticipated from the work of Wood and Hodgkiess

(ref. 3). At 800°C , both NiO and Cr_2O_3 were formed initially (see fig. 7); but the NiO intensity was much greater and was plotted on a separate scale, as was the nickel solid solution. NiO seems to be by far the major oxide. At about six-tenths of an hour, the Cr_2O_3 intensity diminished and the NiO began to level out. At the same time, NiCr_2O_4 began to form. This indicates a reaction of NiO and Cr_2O_3 to form NiCr_2O_4 . This reaction slowed rapidly after 2 hours and the NiO and Cr_2O_3 , which had lost intensity, began to gain. The ThO_2 intensity diminished steadily throughout, indicating that little, if any, of this oxide was incorporated into the scale.

The 1000°C data for polished material (fig. 8) show effects similar to the 800°C data. Once again a large amount of NiO was formed initially. However, by the time the first data were taken, appreciable amounts of NiCr_2O_4 were already present. With time, the Cr_2O_3 and NiCr_2O_4 curves increased, while NiO decreased. At 100 hours, NiCr_2O_4 was still increasing but was less intense than the others. The ThO_2 intensity was similar to that at 800°C . After about 25 hours, the Cr_2O_3 showed a tendency toward a (104) texture.

At 1200°C , similar processes are at work (see fig. 9). Indeed, they were carried further so that, at the end of 100 hours, NiCr_2O_4 appeared to be a major oxide. At this temperature the Cr_2O_3 showed even more of the tendency toward a (104) texture which started in the first hours. In addition, the NiO showed a very strong (100) texture. This texture appeared to be strong from the beginning and got stronger with time. As was the case at 800° and 1000°C for polished samples, the ThO_2 intensity slowly diminished with time. Fortunately, even at the highest temperature and longest time the signal from the nickel solid solution (plotted on the right-hand scale of fig. 9) was quite strong. This indicates that penetration of the oxide layer occurred at all times.

Room-temperature X-ray diffraction (XRD), electron microprobe analysis (EMP), and metallography. - Room-temperature XRD on the scraped oxides, a more sensitive test for minor phases, did not reveal any phases not previously found by HTXRD. The metallography and the following figures are from the HTXRD samples but identical results were obtained from the ΔW samples. Figures 10 and 11 show microstructures of oxidized specimens that were either polished (fig. 10) or ground (fig. 11) before exposure. All samples had been exposed for 96 hours at the indicated temperatures.

The 0.100-inch (0.254-cm) thick TD-NiCr starting material contained approximately 0.372 percent oxygen, which is more than can be accounted for by the ThO_2 . The excess oxygen content is evidenced by the frequent presence of easily visible individual Cr_2O_3 particles and of rows of Cr_2O_3 particles parallel to the rolling direction of the sheet (as shown in figs. 10(b), (c), and (d)).

When TD-NiCr was polished before air oxidation testing at 800°C , the scale that developed after 96 hours of exposure was dark green on the surface and appeared somewhat different over the grain boundaries of the TD-NiCr, as shown in figure 10(a). While the outer surface of the scale was relatively flat, the oxidation front between the

scale and the TD-NiCr was wavy in character (fig. 10(b)). Under polarized light this scale was two-layered. The inner layer was brown. The outer layer was green. Similar results were observed on polished TD-NiCr after 1000^o C exposure for 96 hours. Again the surface was rather smooth. When viewed in cross section (fig. 10(c)), the inner layer was brown and the outer layer was green. Further clarification of the nature of such scales was obtained by an electron micrographic study. At $\times 11\,000$, the scale shown in figure 10(c) can be more clearly observed in figure 12. The electron micrograph shows a light inner phase bordered by islands of a darker phase. The external part of the scale also appears light. Ammonium hydroxide, a selective etch for NiO, attacked mainly outer portions of the scale, which indicated that a portion of the green scale was NiO. The darker phase then was probably spinel and the inner layer, which was not attacked, can still be considered to be the Cr₂O₃.

In an effort to establish more clearly the identity of the three layers shown in figure 12, EMP scans were made across the oxides of the 1000^o C and 1200^o C polished samples. The results are indicated in figure 13. Clearly, the NiO was at the gas-oxide interface and the Cr₂O₃ was at the oxide-metal interface. That the spinel was in between is not as clear because of the small thickness of this layer. Nevertheless, several other similar traces tend to support the fact that the NiCr₂O₄ was located between the NiO and Cr₂O₃, as would be expected. It is the reaction product of NiO and Cr₂O₃. An additional scan was made to check the location of the ThO₂ (see fig. 13). Apparently, the ThO₂ was not present in the NiO. As has been discussed previously, the NiCr₂O₄ layer was too small for it to be determined whether any ThO₂ was present there.

After 96 hours at 1200^o C, figure 10(d) shows that a relatively heavy scale ($>6\ \mu\text{m}$) developed which was similar to, but less smooth than, those found at the lower temperatures.

Comparison of figures 10(b) to (d) indicates a general agglomeration of the Cr₂O₃ that was originally present in the TD-NiCr as an unwanted phase. No internal porosity developed in these specimens. Such porosity has been previously observed in specimens that have been thermally cycled during oxidation testing (see ref. 7). While the porosity that develops in TD-NiCr is still unexplained, cycling may promote its formation.

The effect of grinding on surface topography appeared to remain long after the initial phases of oxidation. For example, figure 11(a) shows that the grinding marks were faithfully replicated by the growing oxide film after 96 hours at 1000^o C. A cross-sectional view of the 96-hour 1000^o C specimen is shown as figure 11(b). The oxide was very thin and jagged as compared to that shown in figure 10(c), which was formed under the same conditions. The oxide peaks correspond to those in the metal surface. Also, under polarized light, only dark green Cr₂O₃ was observed. Agglomeration of the Cr₂O₃ contamination in the alloy matrix had occurred in this specimen also.

The ground specimen exposed for 96 hours at 1200^o C is shown in cross section in figure 11(c). It was similar to the 1000^o C specimen but the peaks in the oxide scale no

longer coincided with the unevenness of the substrate. Here either the scale peaks remained fixed while the substrate surface was smoothed out by horizontal diffusion or the peaks were somehow related to evaporative loss of Cr from the scale. The substrate shows very large internal Cr_2O_3 particles, indicating continued agglomeration of this contaminant. Furthermore, again there is no porosity developing in the alloy matrix. Porosity was observed in samples that were cycled during oxidation testing at elevated temperatures.

Oxidation of Tophet-30

Weight change (ΔW). - The results of weight-change experiments are shown in figure 14. For comparison, curves are shown which were calculated from the parabolic rate data on "pure" Ni-30Cr of Barrett (ref. 5) and from the data of Wood and Hodgkiss (ref. 3) for Ni-27Cr. From these data, Tophet-30 would appear to have superior oxidation resistance to either of these materials. Possible differences in internal oxidation or Cr_2O_3 volatility make such a judgment somewhat uncertain. The data do show that there was little difference in oxidation rates of Tophet-30 for the two surface preparations used.

Thickness change (Δt). - An attempt was made to use the change in metal thickness as a measure of the relative merit of TD-NiCr and Tophet-30. Little difference was found between the ground Tophet-30 and ground TD-NiCr even at 1000 hours at 1200°C (see table II). This indicates that the two Cr_2O_3 formers oxidize at nearly the same rate.

At long times and high temperatures, internal oxidation affected a considerable portion of the Tophet-30 sample (see fig. 18). The extent of this effect is shown in the last column of table II. At 1200°C , much less metal was lost by external scale formation than was affected by internal oxidation.

High-temperature X-ray diffraction (HTXRD). - The oxidation behavior of Tophet-30 is considerably simpler than that of TD-NiCr. At all stages, Cr_2O_3 was the dominant oxide. At 800°C , a small amount of NiCr_2O_4 was detected at all times (see fig. 15) on a polished sample. In addition, early in the oxidation process a small amount of another phase was found but was not present in sufficient quantities to allow identification. It disappeared (due to overlaying of Cr_2O_3) after 10 hours. At 1000°C , the HTXRD pattern is even simpler (see fig. 16). Cr_2O_3 was the only oxide until 50 hours, when small amounts of α -cristoballite (SiO_2) were found. At 1200°C , Cr_2O_3 was still the major oxide (see fig. 17). However, at times longer than 2 hours, the intensity of the Cr_2O_3 began to fall, and NiCr_2O_4 and α -cristoballite (SiO_2) began to appear. It is usually believed that both NiO and Cr_2O_3 are needed before NiCr_2O_4 can be formed. Since NiCr_2O_4 was found without NiO, either this is an exception or the amount of NiO was

below the limits of detectability of the diffractometer. The loss in Cr_2O_3 intensity is probably due both to loss by volatility of Cr_2O_3 and reaction to form NiCr_2O_4 . Again, as in the TD-NiCr, the Ni solid-solution pattern was present at all times and temperatures, assuring penetration of the oxide layer.

Since the polished samples already formed Cr_2O_3 , there was no reason that ground samples should be expected to form any other major oxide. This was shown to be true by room-temperature XRD of the ΔW samples. Therefore, no HTXRD runs were made on ground Tophet-30.

Room-temperature X-ray diffraction (XRD) and metallography. - As in the case of TD-NiCr, scraping the oxide and running room-temperature XRD revealed no phases not previously found by HTXRD.

After 100 hours at 800°C , only a very thin, green surface scale was observed under polarized-light microscopy on the polished Tophet-30. There were a few islands of brown or black, indicating a spinel which is probably NiCr_2O_4 . Grain boundaries of the original substrate could still be seen because of the apparent differences in the oxidation rates of the grains and the grain boundaries. Similar oxide-composition observations were obtained on cross sections of the exposed specimens (fig. 18). In addition, the substrate contained amounts of carbide precipitates, which were mainly concentrated at the grain boundaries.

Exposure of polished Tophet-30 at 1000°C for 96 hours resulted in rough, lumpy scale which exhibited mostly green Cr_2O_3 with some dark brown islands (probably a spinel, NiCr_2O_4) when viewed under polarized light. A cross section of this specimen shows the scale in figure 18(b). This figure also shows that grain-boundary oxidation proceeded in some cases to a depth of 6 mils (0.015 cm). Some of the grain-boundary carbides appear to have gone into solution and matrix grain growth has occurred. Sporadic internal oxidation can be observed throughout the specimen cross section.

Figure 18(c) shows the polished Tophet-30 after 96 hours at 1200°C . The inner portion of the scale is green Cr_2O_3 under polarized light; while the outer portion of the scale is the brown spinel, probably NiCr_2O_4 . This exposure produces extensive internal oxidation in the substrate. Most of the internal oxides are white under polarized light and thus may include both SiO_2 and some ZrO_2 . Very few grain-boundary carbides are left. At this temperature, however, few grain-boundary oxides were observed. Thus, it may be that the grain-boundary carbides dissolve rapidly enough to eliminate the favorable conditions which lead to grain-boundary oxidation.

Similar microstructures were observed on specimens ground on all surfaces before oxidation exposure. Figure 18(d) shows the cross section of such a ground specimen after 100 hours at 1200°C . The main features of oxidation of polished and ground Tophet-30 were as follows:

- (1) The scales formed on all specimens regardless of surface treatment appeared to contain only the green Cr_2O_3 phase when viewed under polarized light.

(2) The depth and extent of internal oxidation appeared to be less in the ground specimens. This may be related to either the rapidity with which they initially oxidize or the nature of the initial scale formation and composition.

(3) There appeared to be less grain-boundary oxidation in the ground specimens, which may well be related to the same factors mentioned in (2).

Oxidation Process of TD-NiCr and Tophet-30

From the preceding results, it is apparent that an explanation of the mode of oxidation of TD-NiCr which does not include a consideration of surface preparation is incomplete. The mechanism by which the initial surface controls oxidation is not known. It has been demonstrated however, that surface effects do influence the scales formed. Furthermore, these effects are important over a wide range of temperatures (800° to 1200° C) and for extended times (over 100 hr). In discussing the oxidation behavior of TD-NiCr, attention is first given to the results obtained with polished surfaces. These probably best represent the intrinsic oxidation of the materials. This is followed by discussion of the ground-surface sample data. Finally, the oxidation of Tophet-30 is compared with that of TD-NiCr.

Figure 19 is a schematic representation of our view of the oxidation of polished TD-NiCr. Stage 1 represents the metal upon insertion into the furnace. At stage 2, NiO has formed concurrently with Cr_2O_3 . As shown, the NiO is on the top, as we know from postoxidation metallography. Apparently the NiO and Cr_2O_3 nucleate at the same time but the NiO grows faster and covers the Cr_2O_3 . While this representation agrees with the observations of Wood and Hodgkiess (ref. 3), it presents a problem in understanding how oxygen is transported through the NiO to allow further growth of the Cr_2O_3 since NiO is a p -type cation-deficient semiconductor. This oxygen transport is not understood, but it may be aided either by interconnected voids in the NiO or diffusion of O_2 through the NiO grain boundaries. The latter seems more likely, inasmuch as no metallographic evidence of holes in the NiO layer was found; but neither explanation may be right. All that is known is that Cr_2O_3 does continue to grow, as shown by the HTXRD data, in spite of the dense NiO overlay.

By stage 3, the NiO and Cr_2O_3 have begun to react to form spinel. Prior to the spinel reaction, NiO dissolved Cr_2O_3 . This solution can be extensive, as shown by Armijo (ref. 14). As a result, stage 4 is reached, in which Cr is transported across the NiO and volatilizes. Thus, the NiO barrier to volatilization postulated by Wood and Hodgkiess (ref. 3) is not realized. Although our microprobe work did not conclusively show the presence of chromium in the NiO layer, Wood and Hodgkiess were positive that they had found chromium in the outer layer of NiO in their work (ref. 3).

In addition to allowing chromium to be lost, the solubility of NiO for Cr at high temperatures may have another deleterious effect; that is, upon cooling, NiCr_2O_4 is precipitated from the NiO (ref. 14), which could be a contributing cause in the tendency for spalling seen in oxidized polished TD-NiCr. The position of the original interface S_0 in figure 19 is inferred from considerations put forth by Armijo (ref. 14) which demonstrate that NiCr_2O_4 formation from the oxides results from countercurrent diffusion of Cr^{+3} and Ni^{+2} .

Grinding of the TD-NiCr prior to oxidation alters the mode of oxidation drastically. Cr_2O_3 is the only oxidation product found, except at the highest temperature (1200°C). Even at 1200°C , the Cr_2O_3 is formed first and NiO only begins to appear after 8 hours and NiCr_2O_4 only after 20 hours. Neither becomes a major phase. Thus, the oxidation of ground TD-NiCr involves a combination of the oxidation of the alloy to form Cr_2O_3 and the subsequent volatilization of the Cr_2O_3 (ref. 10). In the advanced stages of oxidation, enough chromium may be lost to result in the formation of NiO and NiCr_2O_4 . This process could even be accelerated in practical applications where increased gas flow and moist air might be encountered, inasmuch as Caplan and Cohen (ref. 10) found that loss of Cr_2O_3 was accelerated by both moisture and flowing oxygen.

Our representation of the oxidation of Tophet-30 is similar to that of ground TD-NiCr. Cr_2O_3 is the major oxide formed. The only effect of surface preparation is the presence of a minor amount of NiCr_2O_4 in polished samples which is not found in the ground samples. SiO_2 is found as a crystalline phase in both surface preparations at 1000°C and 1200°C , but had little apparent effect on the oxidation.

The lack of influence of surface preparation on the oxides that form on Tophet-30 may be twofold. First, the presence of Si has often been suggested to stabilize Cr_2O_3 formation (ref. 8); and second, the Cr level may already be sufficiently high (30 percent) to ensure Cr_2O_3 being formed first, no matter what the condition of the surface.

Barrett (ref. 5) postulated that Cr_2O_3 is the protective phase in the Ni-Cr system and that once this phase forms exclusively, the maximum oxidation resistance in the system is reached. However, their data showed a minimum in the rate-constant-against-chromium curve near 20 percent Cr and an increase near 100 percent Cr. Recently, Evans (ref. 15) indicated that the increase was due to lack of pure chromium. Use of pure-chromium oxidation data gives the same parabolic rate constant for pure Cr as for Ni-20Cr. This conclusion is borne out by a comparison of TD-NiCr (ground) and Tophet-30, which shows little real difference between the oxidation rate of the two alloys based on thickness loss of the metal. This is in contradiction to the weight-gain data, which show an increase in rate of the Tophet-30 over the TD-NiCr. This is actually due to either internal oxidation or, more likely, differences in volatility, possibly from impurities such as Si. The presence of such impurities may account for the higher weight gains and nearly parabolic behavior observed in earlier work on 80Ni-20Cr alloys (refs. 5 and 13).

SUMMARY OF RESULTS

The oxidation of TD-NiCr and Tophet-30 was studied in the range 800^o to 1200^o C under static isothermal conditions. The following results were obtained:

1. Metal-thickness loss of TD-NiCr and Tophet-30 due to oxidation at temperatures from 800^o to 1200^o C for times to 1000 hours was slight. Both alloys have excellent isothermal oxidation resistance in static air.

2. Surface preparation has a profound effect in controlling the scales that form on oxidized TD-NiCr at 800^o to 1200^o C.

(a) Polished surfaces oxidized initially to NiO and Cr₂O₃, which subsequently reacted to form NiCr₂O₄.

(b) Ground surfaces oxidized only to Cr₂O₃.

(c) Cr₂O₃ volatilized in both cases and, as a result, markedly reduced the amount of weight gain measured during oxidation.

(d) TD-NiCr with polished surfaces lost slightly less metal during oxidation at 1200^o C than the ground samples, but showed a tendency to spall.

3. Surface preparation of Tophet-30 had little effect on the scales formed during oxidation at 800^o to 1200^o C.

(a) The major oxide formed on Tophet-30 is always Cr₂O₃.

(b) This Cr₂O₃ appears to be less prone to volatilization than that formed on TD-NiCr.

(c) The amount of metal lost due to external scale formation is about the same as with ground TD-NiCr; however, Tophet-30 has extensive internal oxidation at 1200^o C.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, December 28, 1970,
129-03.

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TABLE I. - CHEMICAL ANALYSIS OF TD-NiCr AND TOPHET-30

Element	Content, wt. %		Element	Content, wt. %	
	TD-NiCr	Tophet-30		TD-NiCr	Tophet-30
Cr	21.71	29.63	Al	<0.001	0.3
Th	2.19	(a)	V	(a)	.15
O	.372	.010	Zr	<.001	.04
Ni	Balance	Balance	Ca	<.003	.02
Fe	.003	.15	Co	(b)	.001
Si	.001	1.43	Cu	(b)	.001
N	.131	.084	Mn	<.001	.01
C	.008	.028	P	.0009	.003
S	.010	.007	H	.0001	.0004

^aNot analyzed.^bNot detected by spectrochemical analysis.

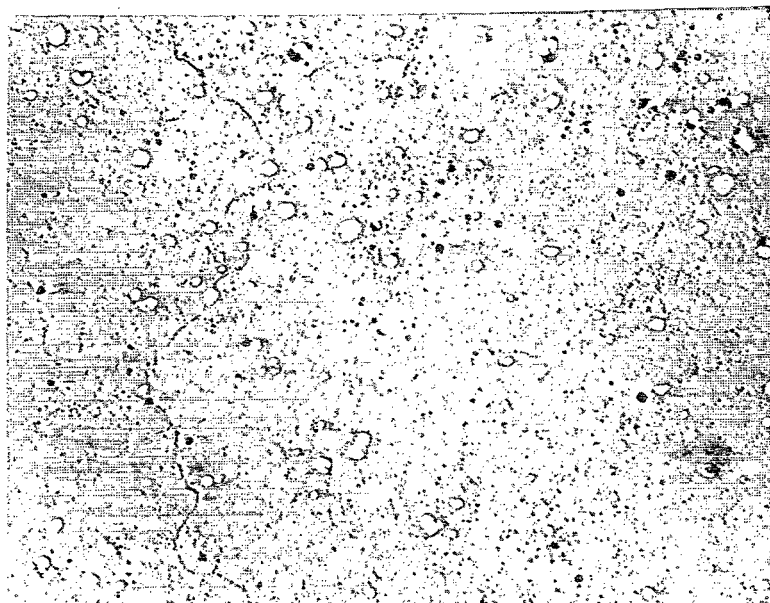
TABLE II. - METAL-THICKNESS CHANGE IN TD-NiCr

AND TOPHET-30 AFTER OXIDATION AT

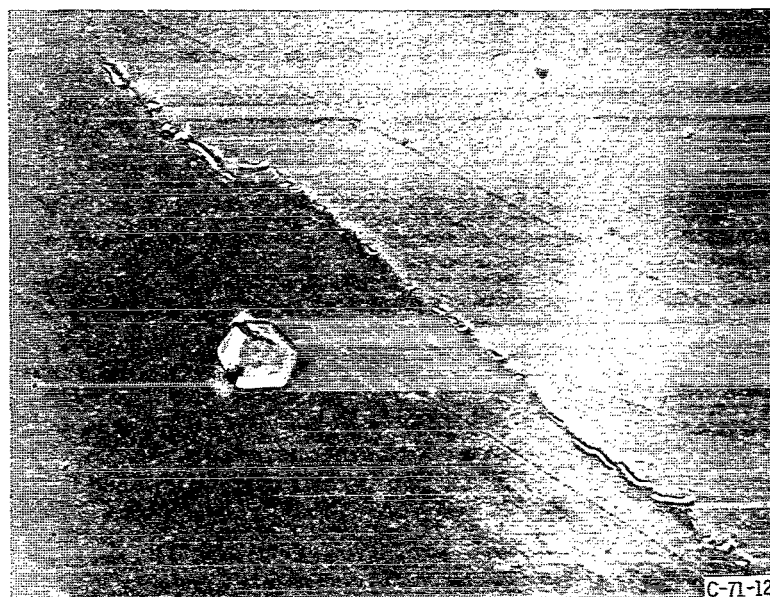
1000° AND 1200° C

Temperature, °C	Time, hr	Metal-thickness change ^a , Δt, μm			
		TD-NiCr		Tophet-30 (ground)	
		Polished	Ground	Scale to scale	Unaffected metal
1000	50	8	1	2	2
	100	11	2	6	6
	200	6	0	8	8
	400	11	12	14	14
	800	8	10	16	82
	1000	8	5	--	--
1200	50	4	15	25	65
	100	4	17	24	122
	200	2	14	46	162
	400	10	23	39	191
	800	16	27	39	279
	1000	21	32	39	314

^aUncertainty, <±5 μm.



(a) TD-NiCr. X11 000.



(b) Tophet-30. X18 200.

Figure 1. - Electron micrographs of TD-NiCr and Tophet-30.

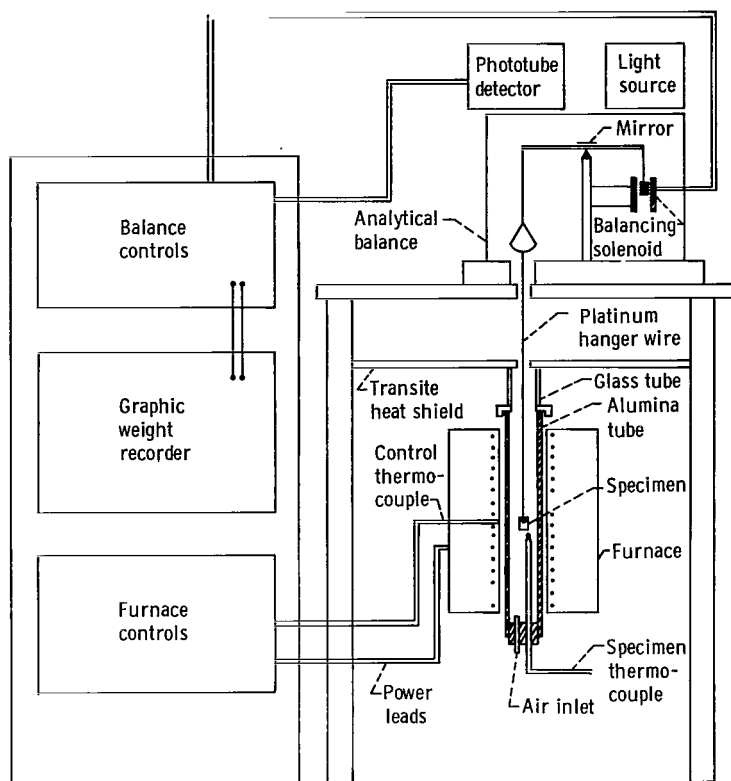


Figure 2. - Continuous-weight-gain apparatus.

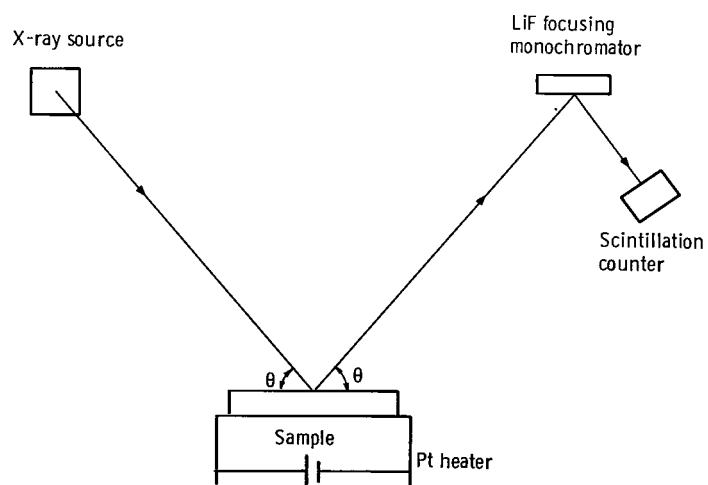


Figure 3. - Schematic diagram of high-temperature X-ray diffractometer.

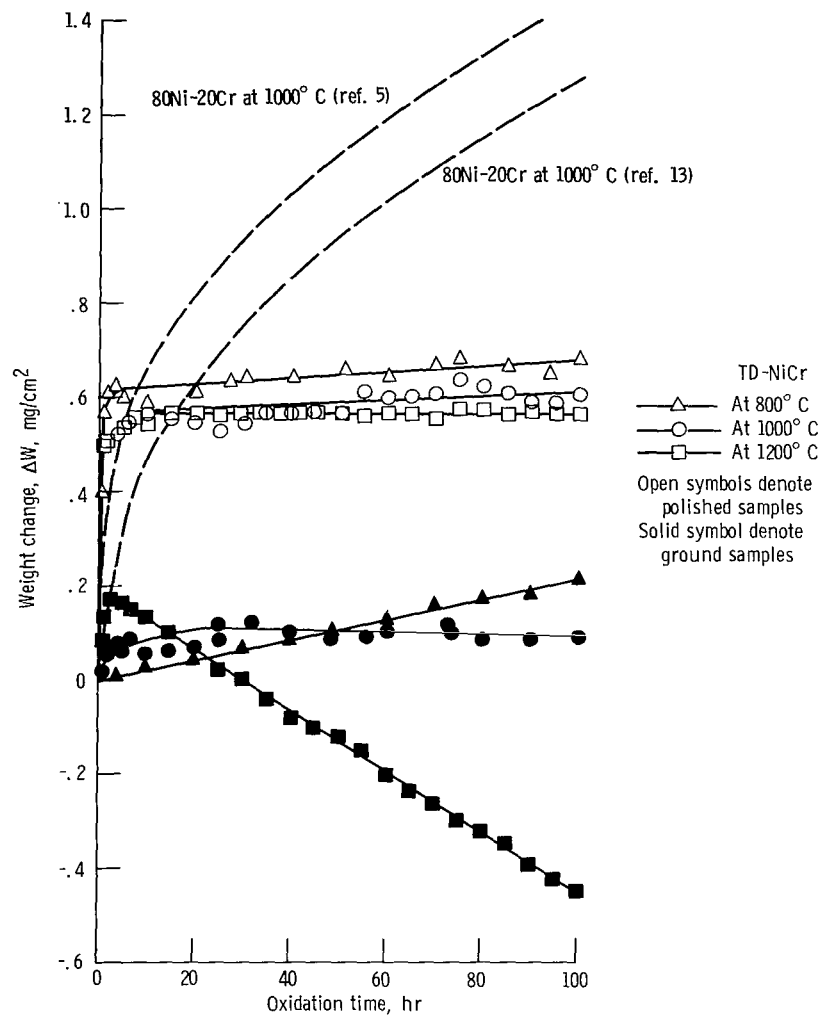


Figure 4. - Weight change in isothermal oxidation of TD-NiCr in air.

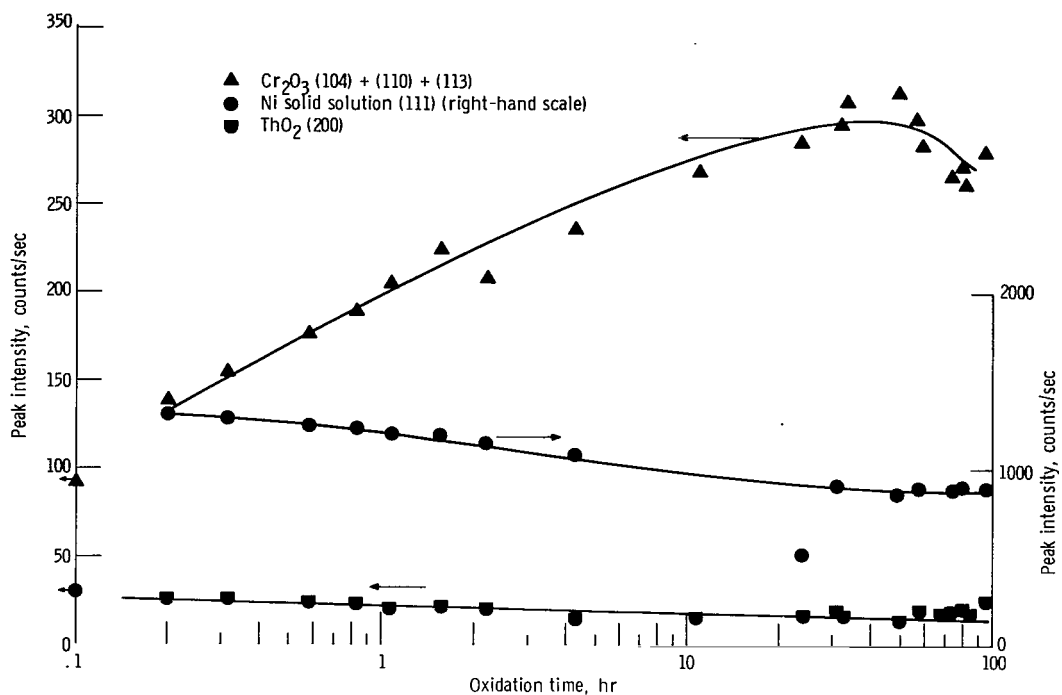


Figure 5. - HTXRD intensities during oxidation of ground TD-NiCr at 1000° C.

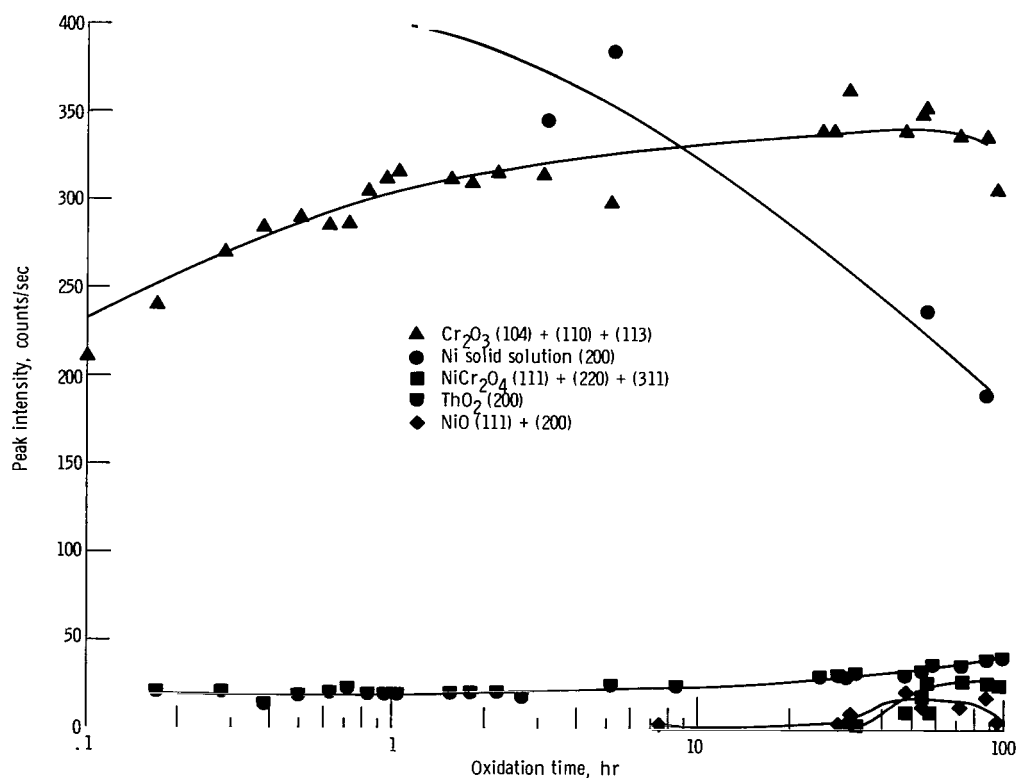


Figure 6. - HTXRD intensities during oxidation of ground TD-NiCr at 1200° C.

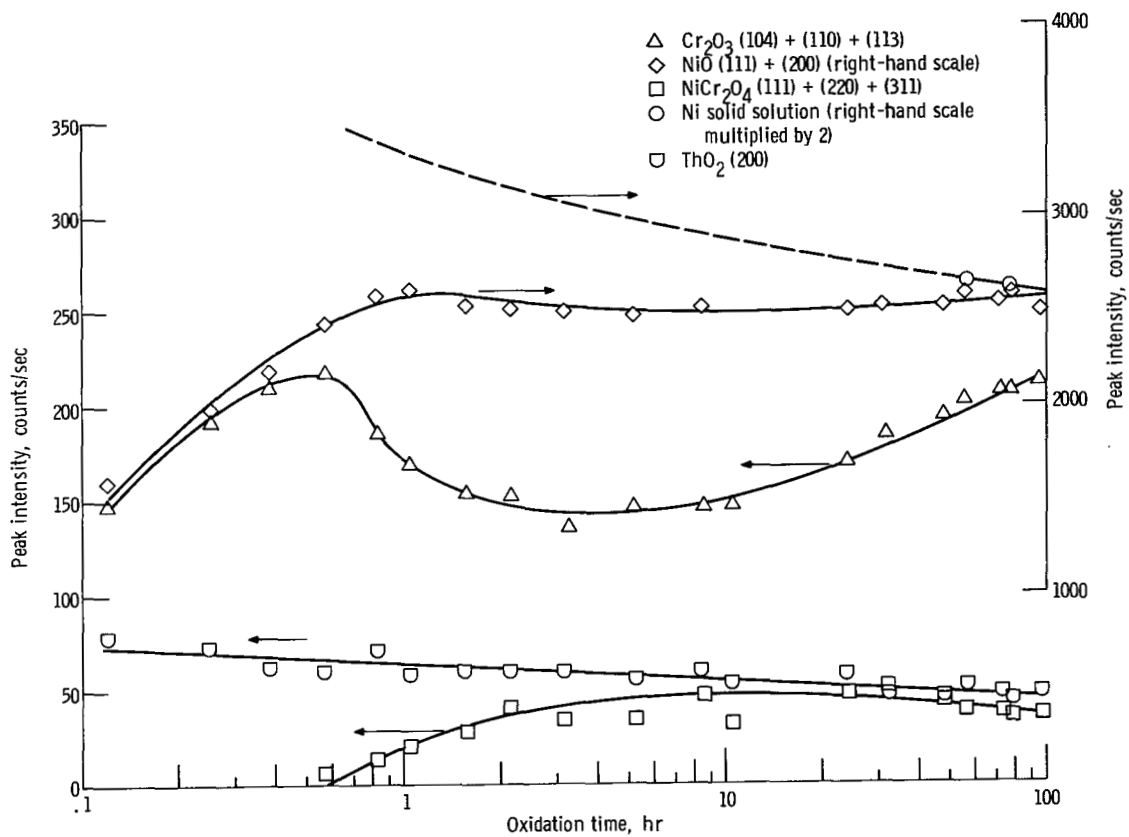


Figure 7. - HTXRD intensities during oxidation of polished TD-NiCr at 800° C.

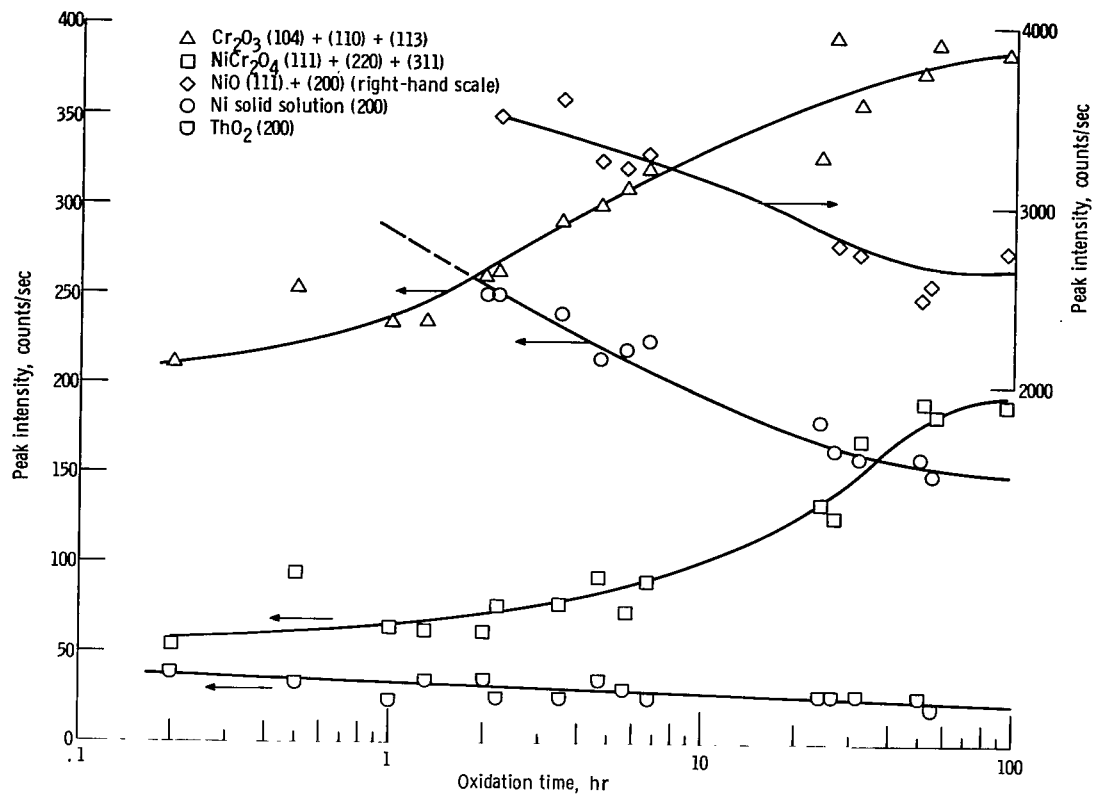


Figure 8. - HTXRD intensities during oxidation of polished TD-NiCr at 1000° C.

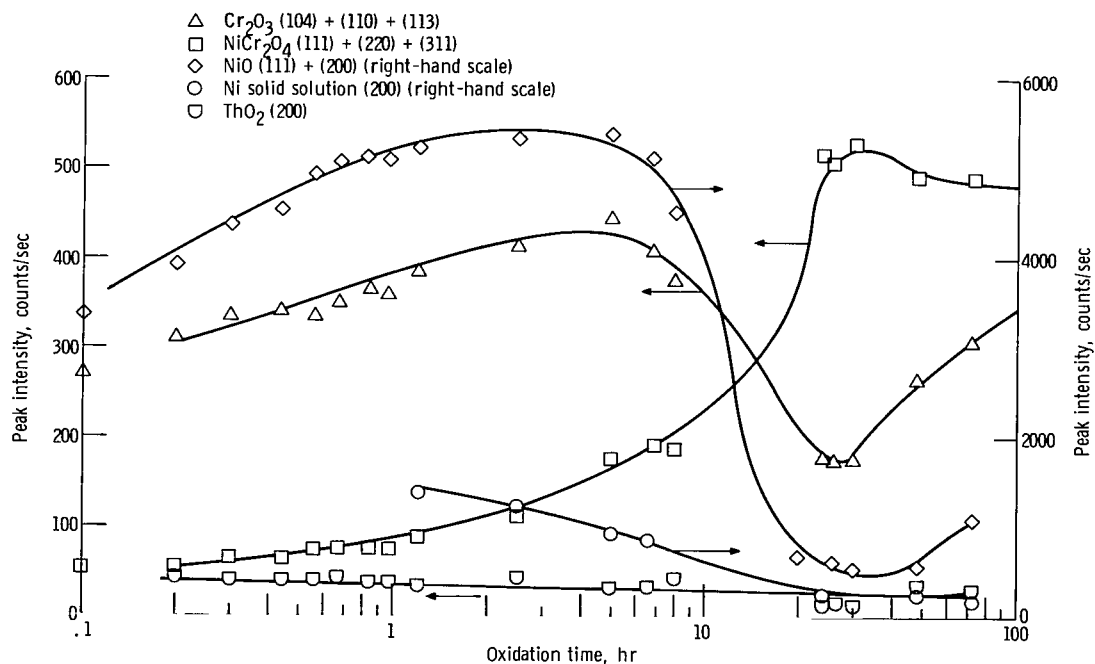
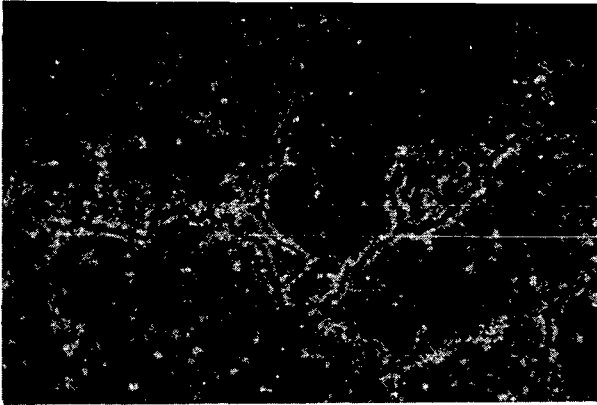
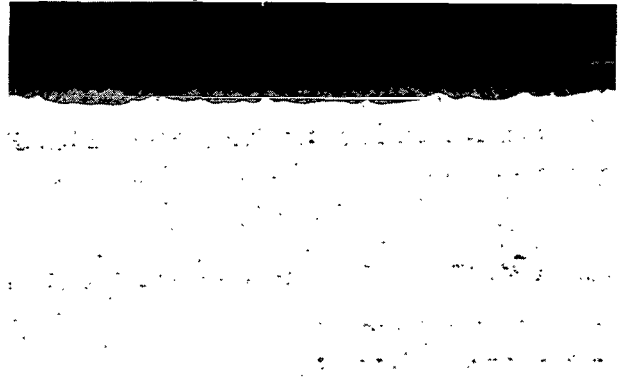


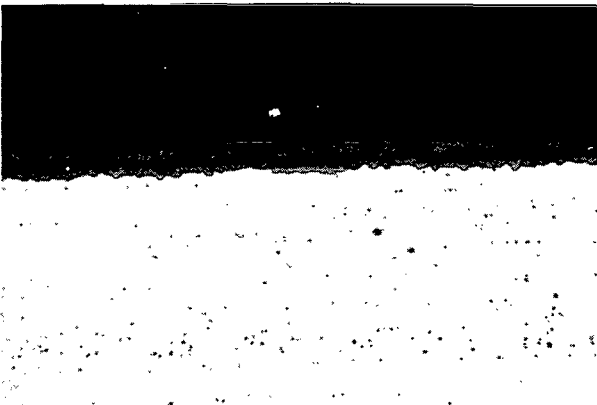
Figure 9. - HTXRD intensities during oxidation of polished TD-NiCr at 1200° C.



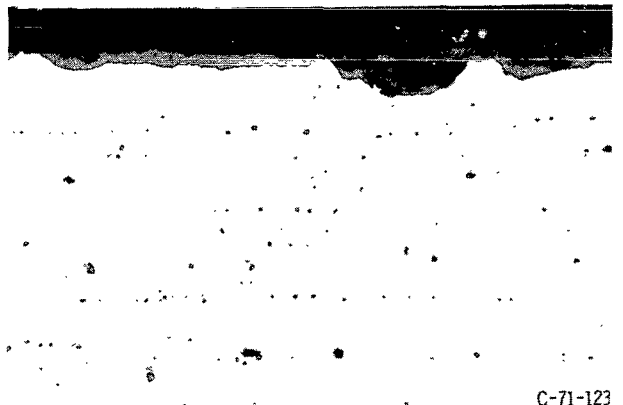
(a) Oxidized at 800° C for 96 hours. View of surface, X250.



(b) Oxidized at 800° C for 96 hours. Cross section, X500.



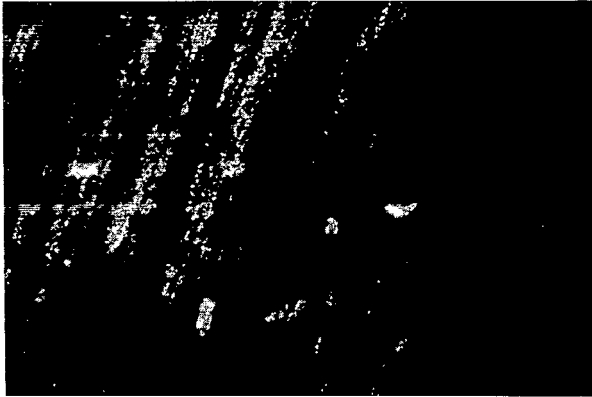
(c) Oxidized at 1000° C for 96 hours. Cross section, X500.



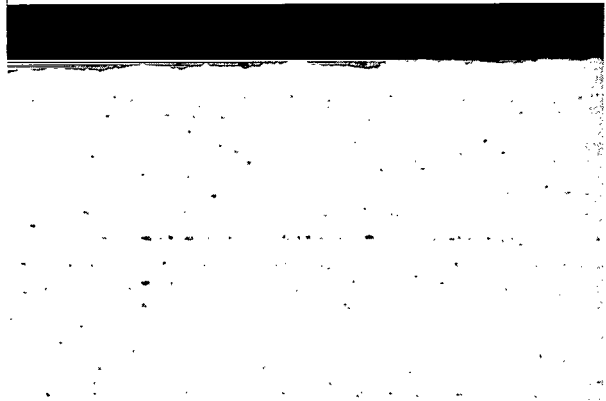
(d) Oxidized at 1200° C for 96 hours. Cross section, X500.

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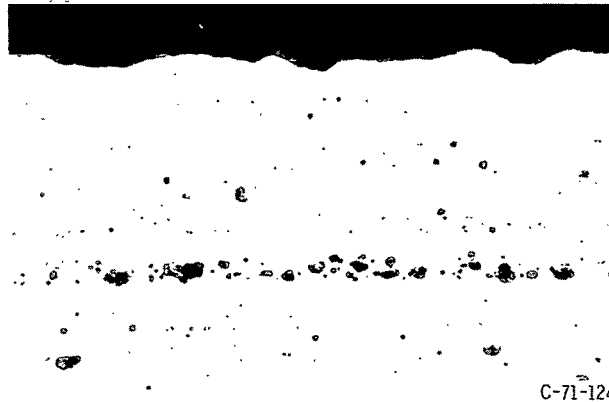
Figure 10. - Metallography of TD-NiCr polished and then oxidized.



(a) Oxidized at 1000° C for 96 hours. View of surface. X250.



(b) Oxidized at 1000° C for 96 hours. Cross section. X500.



(c) Oxidized at 1200° C for 96 hours. Cross section. X500.

Figure 11. - Metallography of TD-NiCr ground then oxidized.

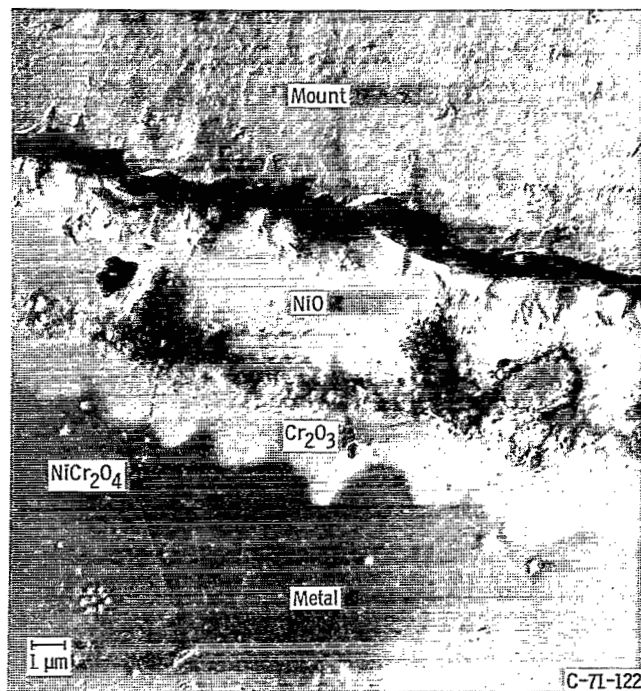


Figure 12. - Electron micrographs of polished TD-NiCr, oxidized at 1000° C for 96 hours. X11 000.

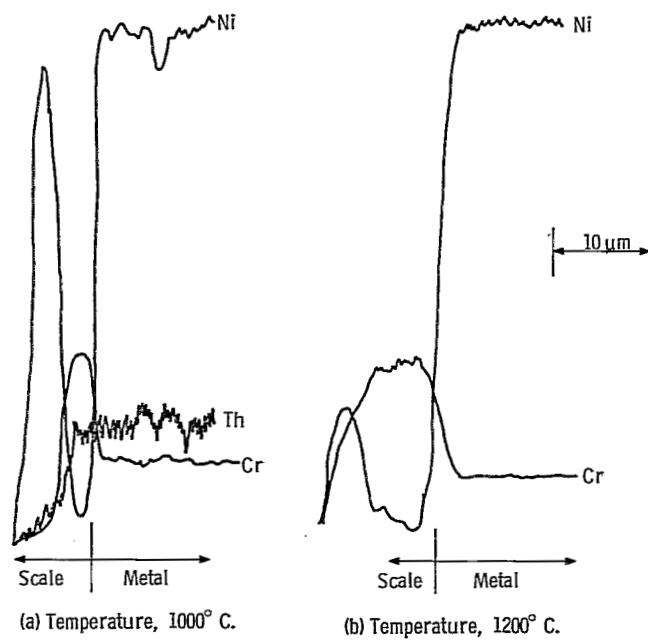


Figure 13. - Electron-microprobe scans on polished TD-NiCr oxidized for 96 hours at 1000° and 1200° C.

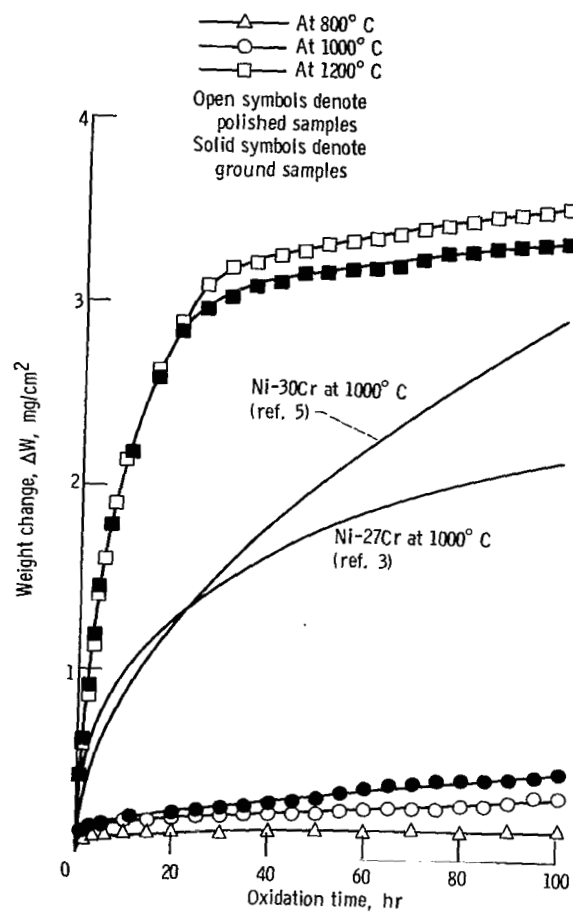


Figure 14. - Weight change in isothermal oxidation of Tophet-30 in air.

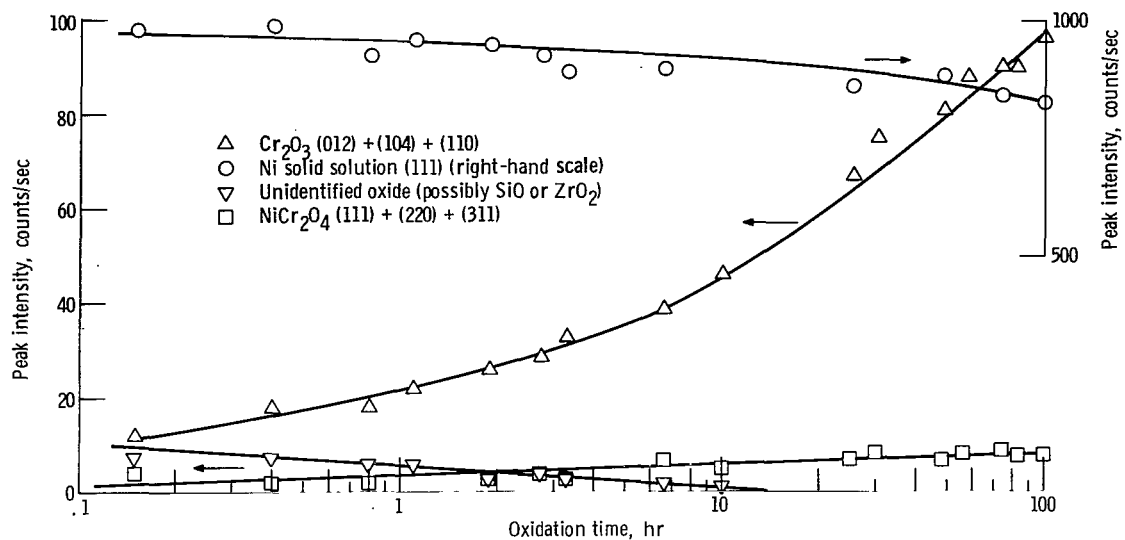


Figure 15. - HTXRD intensities during oxidation of polished Tophet-30 at 800° C.

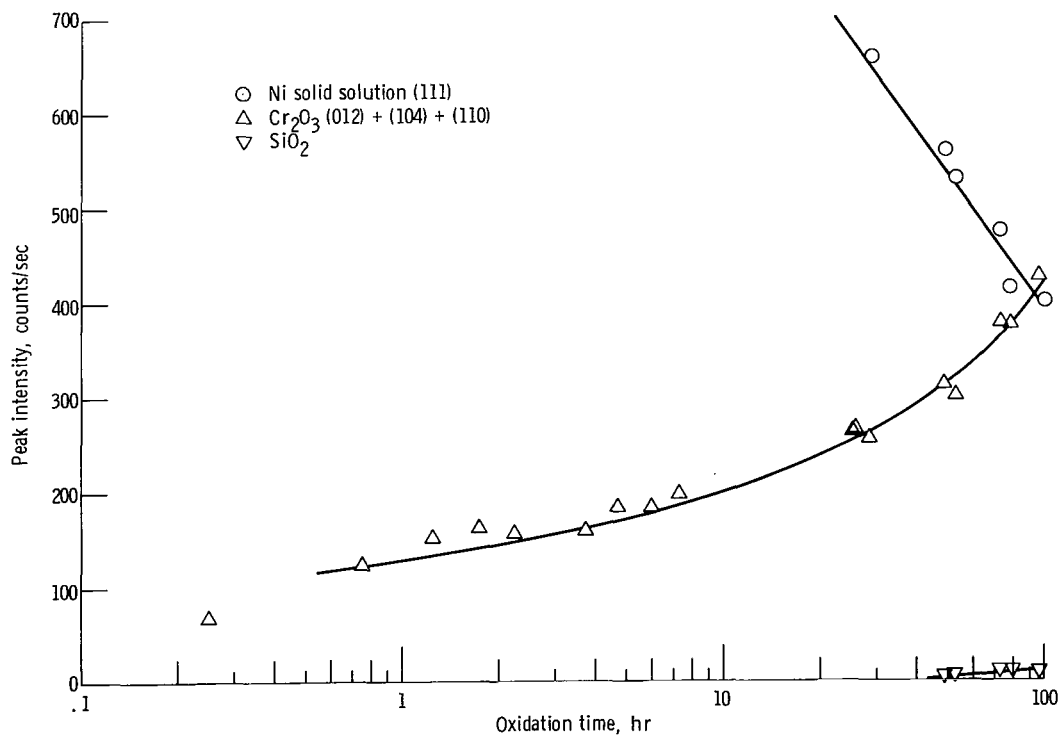


Figure 16. - HTXRD intensities during oxidation of polished Tophet-30 at 1000° C.

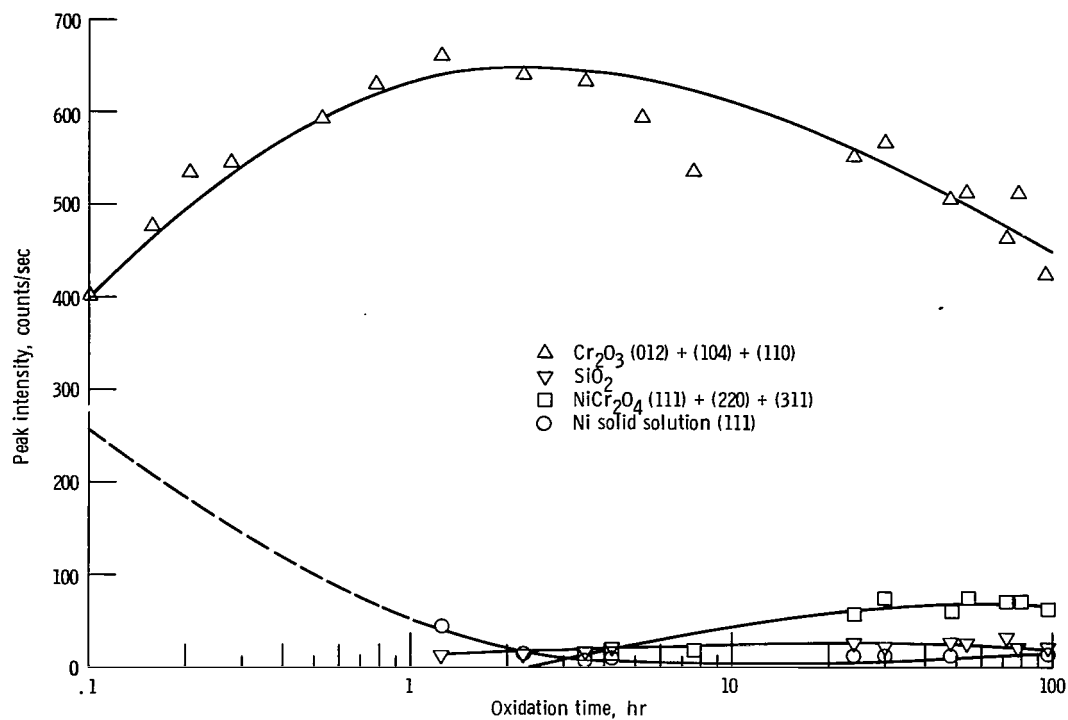
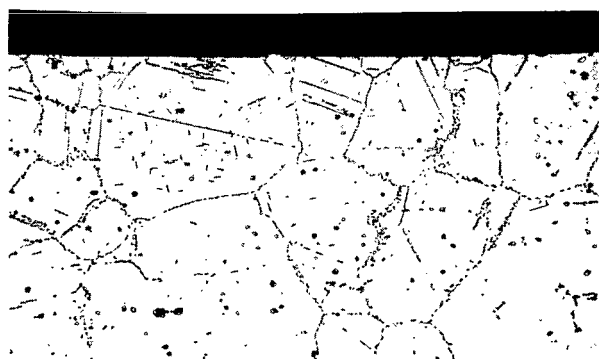
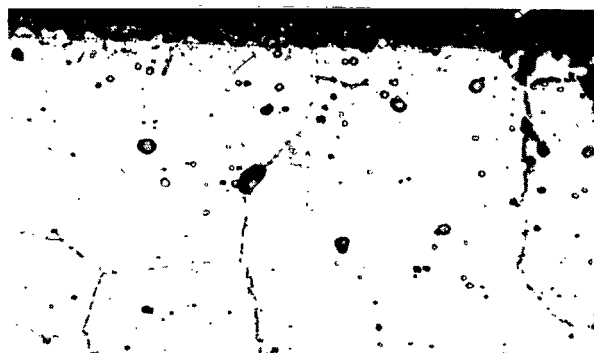


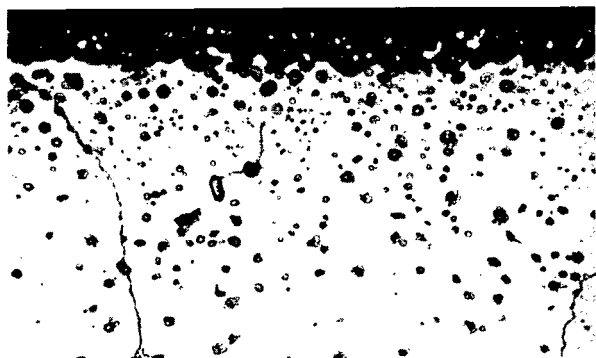
Figure 17. - HTXRD intensities during oxidation of polished Tophet-30 at 1200° C.



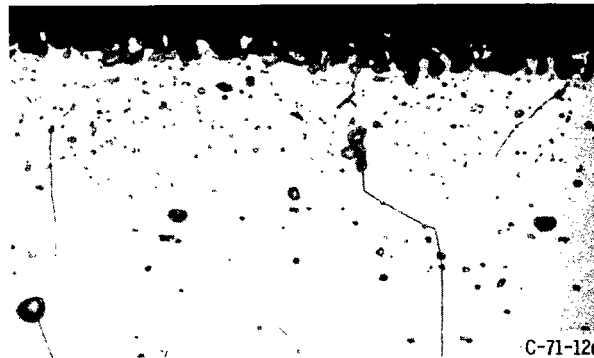
(a) Oxidized at 800° C for 100 hours. Polished. X500.



(b) Oxidized at 1000° C for 100 hours. Polished. X500.

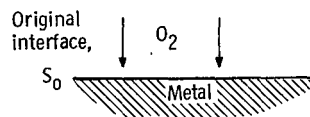


(c) Oxidized at 1200° C for 100 hours. Polished. X500.

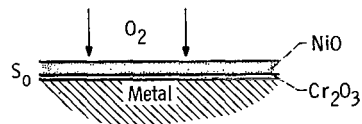


(d) Oxidized at 1200° C for 100 hours. Ground. X500.

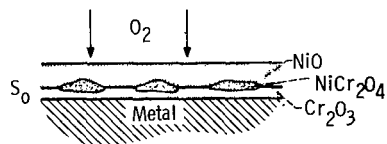
Figure 18. - Metallography of Tophet-30 after oxidation.



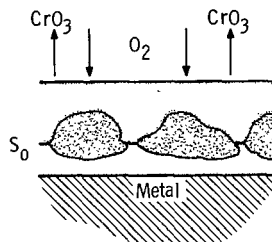
(a) Stage I: sample inserted into furnace.



(b) Stage 2: NiO and Cr_2O_3 form.



(c) Stage 3: Cr_2O_3 dissolves in NiO and $NiCr_2O_4$ forms.



(d) Stage 4: Oxides grow and CrO_3 goes off as a gas.

Figure 19. - Schematic representation of oxidation of polished TD-NiCr.

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